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(54) PROCESS FOR REDUCING THE RESIDUAL CONTENT OF
VINYL CHLORIDE MONOMER IN VINYL CHLORIDE
POLYMERS

(71) We, HOECHST AKTIEN-GESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt (Main) 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for improving the properties of vinyl chloride polymers, and more especially to a process for reducing the residual content of vinyl chloride monomer in such polymers.

As a result of recent investigations into damaging physiological actions of monomeric vinyl chloride that may possibly occur, it is desirable to obtain from this monomer polymers that have a substantially lower content of monomeric vinyl chloride (VC) than was customary hitherto.

In the known industrial processes for manufacturing polyvinyl chloride and those of its copolymers and graft polymers with other monomers or polymers which contain a predominant proportion of polymerised vinyl chloride, the product obtained at the end of the polymerisation process, after releasing the reaction mixture pressure, contains up to 3% by weight of unreacted vinyl chloride.

If the reaction products of the emulsion or the suspension polymerisation are in the form of a dispersion of the polymer in water, the residual monomer content can be reduced by treatment of the product with water vapor or heated inert gases for example, as described in U.S. Specifications Nos. 3,469,617 and 3,371,059 and in German Specifications Nos. 1,029,155, 1,248,943, 2,414,625 and 2,435,704. Various processes have been proposed for carrying out such treatment. In some processes the aqueous dispersion is intimately mixed with the water vapor simply by conveying the two together in a tube or by spraying the dispersion in a steam atmosphere.

After a relatively short or long contact time, this mixture, optionally with additional heating through the container walls, is separated again into the gaseous phase containing monomer and into an aqueous polymer dispersion having a reduced monomer content. It has also been proposed in German Specification No. 1,026,525 to remove the monomer content by passing water vapor in countercurrent to the aqueous polymer dispersion in a column or, as in German Specification No. 2,162,860, to treat the dispersion with inert gas in a pipe evaporator.

Another previous proposal for removing residual monomer from aqueous dispersions of vinyl chloride polymers described in German Specifications Nos. 2,429,777 and 2,527,583 involves vaporising certain quantities of water for at least 15 minutes at 150 to 650 torr. In yet another process, slurries or latices of vinyl chloride polymers are either heated to temperatures of 70 to 125°C or brought into contact with at least one organic liquid at temperatures of 25 to 125°C and the monomer removed from the slurries.

It has furthermore been proposed, in German Specification No. 2,527,584, to remove residual monomers by water-vapor treatment of moist vinyl chloride polymerisation products obtained by emulsion or suspension polymerisation.

All these previous processes are concerned with mixtures of polymer and water either in the form of aqueous dispersions, in which the proportion of water is greater than the proportion of polymer, or in the form of moist products as produced, for example, by decanting aqueous polymerisation products of suspension polymerisation and possessing, generally, a water content of 15 to 35% by weight.

Some of the processes mentioned above require considerable expenditure on apparatus. Also, in the case of the short process (duration of treatment a few seconds to a few minutes) the monomer removal effect is

generally inadequate. Further, in processes involving the degassing of aqueous dispersions, difficulties may arise as a result of foaming, either necessitating additional expenditure on apparatus or the addition of special agents which increase the costs and may also influence the end product in an undesirable manner. All of the processes mentioned require a relatively large amount of energy since, in some cases, apart from the polymer, considerable quantities of water must be heated or evaporated. They are furthermore not very well suited to polymers that are produced without water, for example, by bulk or gas phase polymerisation.

To remove residual monomers from dry vinyl chloride polymers, namely those that have been obtained by bulk or gas phase polymerisation, a process has been proposed, in German Specification No. 2,331,895, in which water vapor is condensed onto the dry polymer and, after this condensed water has acted for some time, it is evaporated again by the action of heat. As a result, however, of the addition of water by means of condensation an important advantage of the so-called "dry" polymerisation process, that is, being able to dispense with separating the water by filtration and/or drying, is lost. In addition, it is clear that only polymers having a residual monomer content of above 0.01% by weight of vinyl chloride can be produced according to this process and these do not meet the recent ideas put forward for a physiologically tolerable polyvinyl chloride (at most 0.001% by weight of residual vinyl chloride or less).

It is an object of the present invention to provide a process which is capable of reducing to a very low level the residual contents of monomeric vinyl chloride in substantially dry vinyl chloride polymers, and does not suffer to the same extent from the above-mentioned disadvantages.

The present invention provides a process for the treatment of a polymer composition comprising a homo-, co- or graft polymer product containing at least 50% by weight of polymerised vinyl chloride units (based on the total weight of the composition) and the composition including monomeric material and optionally water, which process comprises removing from the composition the main quantity of unreacted monomeric material and, if present, water, and thereafter subjecting the composition in a particulate state to a heat treatment to reduce its residual content of vinyl chloride monomer, the heat treatment being carried out at a temperature in the range of from 75° to 120°C for a period of from 10 minutes to 6 hours and in the presence of a total of from 0.01 to 5% by weight (based on the dry polymer product) of at least one aliphatic, saturated or unsaturated, branched or unbranched compound which con-

tains two or more free hydroxyl groups and at least two carbon atoms and which, in the case of a compound containing four or more carbon atoms, may contain at least one C—O—C link.

The removal of the main quantity of the unreacted monomer or monomers can be carried out according to known processes by relieving the pressure of the polymerisation mixture. If the polymer has been produced by bulk or gas-phase polymerisation and is already dry, it is generally subsequently evacuated. The vacuum is then removed with an inert gas. If the polymer has been produced in aqueous suspension, the separation of the water is carried out, after relieving the pressure of the polymerisation mixture, for example, by decanting and drying in an air current. In all cases a pulverulent polymer is obtained which generally still contains 1 to 0.1% by weight of residual monomer(s).

The subsequent heat treatment according to the invention is preferably carried out under atmospheric pressure or at a reduced pressure. The treatment is advantageously carried out at 50 to 760 torr, more especially at atmospheric pressure. In the course of the treatment one or more inert gases such as air, nitrogen and water vapor, or mixtures of at least two of the gases air, nitrogen and water vapor are advantageously passed through the vessel in which the treatment is carried out. The treatment atmosphere more especially comprises air.

The concentration of the monomeric vinyl chloride in the polymer product decreases as the temperature and the duration of the treatment increase. In the process of the invention, the treatment time is at least 10 minutes. With higher temperatures and longer treatment times undesirable discolouring of the polymer might be expected to increase, with the result that polymers treated in this way might be expected to be strikingly unattractive, particularly in thermoplastic processing, because only moulded articles with discolorations can be produced. In the absence of compounds having 2 free OH groups and 2 to approximately 24 carbon atoms, used in accordance with the invention, such discolourations occur prematurely and, as a result, extensive removal of the residual monomer would be possible either only imperfectly or only by accepting undesired discoloration. If the heat treatment is carried out in the presence of one or more of the specified aliphatic compounds it is possible to increase the treatment time and temperature.

Above 120°C temperature and above 360 minutes treatment time the process would offer no further advantages in practice, since beyond these conditions the particle variations become too pronounced and discoloration occurs. Particularly good results are obtained if the treatment is carried out at 80 to 100°C.

Advantageously the heat treatment is car-

ried out in such a manner that the product of treatment temperature ($^{\circ}\text{C}$) (or, where the treatment temperature varies, the average treatment temperature), and treatment time (hours) is 25 to 350 ($^{\circ}\text{C}\cdot\text{h}$) and especially 50 to 260 ($^{\circ}\text{C}\cdot\text{h}$).

Below 0.01% by weight the beneficial action of the aliphatic compounds would be no longer apparent; above 5% by weight addition, the disadvantages of such additions as a result of a deterioration in the pourability of the polymer powder, reduction in the heat resistance and transparency of the moulded articles produced from the polymer, as well as adhesion to the parts of the processing machine, would outweigh the advantages. Advantageously, the total proportion of the aliphatic compound or compounds is from 0.2 to 2% by weight and especially 0.5 to 1.5% by weight (calculated on the dry polymer product, that is to say, the polymer composition excluding water and monomer).

The or each aliphatic compound may be added to the reaction mixture before or during the polymerisation of the vinyl chloride or may be added, after polymerisation, to the finished polymer before the heat treatment. For the purpose of better distribution in the finished polymer the compound(s) may be added diluted with, or dissolved in, a readily volatile solvent, for example water.

Excessive dilution with water should be avoided, however, since in the presence of relatively large amounts of water, commencing at approximately 5% by weight of water calculated on the dry polymer, the effect according to the invention is diminished and discoloration occurs increasingly the higher the quantity of water.

The compounds to be used in accordance with the invention may contain $\text{C}-\text{O}-\text{C}$ bonds, that is, ether-oxygen bridges. Good results are obtained with compounds of the formula



in which

$\text{X}=\text{H}$ and/or CH_3- ; and
 n = an integer from 1 to 12.

Diglycol or triglycol or a mixture of diglycol and triglycol are especially suitable for the heat treatment according to the invention.

Good results are also obtained if the heat treatment is carried out in the presence of one or more aliphatic, saturated or unsaturated, branched or unbranched compounds having 2 or more free hydroxyl groups, 3 to 12 carbon atoms, and do not contain ether-oxygen bridges.

There may be mentioned as examples of such compounds: 1,3-propanediol; 1,4-butane-

diol; 1,6-hexanediol; 1,5-pentanediol; 2,5-hexanediol; 1,10-decanediol. Particularly good results are obtained with 2-butene-1,4-diol.

The heat treatment of the invention may be carried out in the presence of one of the aliphatic compounds alone, or a mixture of two or more of the compounds may be used.

The incorporation of the aliphatic compound(s) before or during polymerisation does not noticeably alter the quality or the nature of the polymer particles produced. Moreover, all substances that are advantageously used and are customary in polymerisation may be used in conjunction with the aliphatic compounds used in accordance with the invention.

Dry vinyl chloride homo-, co- or graft polymer compositions produced by emulsion or suspension polymerisation may be subjected to the treatment according to the invention. Preferably, however, the polymer has been produced in the gas phase and, more especially, by bulk polymerisation, particularly at temperatures of 30 to 85°C . All the polymerisation processes mentioned may be carried out continuously or in batches.

Vinyl chloride homo- or copolymer compositions having a content of at least 80% by weight (calculated on total composition) of polymerised vinyl chloride units, especially homopolymers with a content of at least 98% by weight (calculated on total composition) of polymerised vinyl chloride, are especially suitable.

Examples of monomers which may be copolymerised with vinyl chloride include the following: olefins such as ethylene or propylene; vinyl esters of straight-chained or branched carboxylic acids having 2 to 20, preferably 2 to 4 carbon atoms, such as vinylacetate, vinylpropionate, vinylbutyrate, vinyl-2-ethylhexanoate, vinylisotridecanoic acid esters; vinyl halides, such as vinyl fluoride, vinylidene fluoride, vinylidene chloride; vinyl ether, vinyl pyridine; unsaturated acids, such as maleic, fumaric, acrylic, and methacrylic acids and their mono or diesters with mono or dialcohols having 1 to 10 carbon atoms; maleic anhydride; maleic acid imide and its N-substitution products with aromatic, cycloaliphatic and optionally branched, aliphatic substituents; acrylonitrile and styrene.

There may be used for graft polymerisation, for example, elastomeric polymers obtained by the polymerisation of one or more of the following monomers: dienes, such as butadiene and cyclopentadiene; olefins, such as ethylene and propylene; unsaturated acids, such as acrylic or methacrylic acid and the esters of such acids with mono or di-alcohols having 1 to 10 carbon atoms; styrene; acrylonitrile; vinyl compounds, such as vinyl esters of straight-chained or branched carboxylic acids having 2 to 20, preferably 2 to 4, carbon atoms, vinyl halides, such as vinyl chloride and vinylidene chloride.

The polymerisation can be carried out with or without a seed polymer in the presence of 0.001 to 3% by weight, preferably 0.01 to 0.3% by weight, calculated on the monomers, of radical-forming catalysts, such as, for example, diaryl and diacyl peroxides, such as diacetyl, acetylbenzoyl, dilauroyl, dibenzoyl, bis-2,4-dichlorobenzoyl and bis-2-methylbenzoyl peroxides; dialkyl peroxides, such as di-tert.-butyl peroxide; peresters, such as tert.-butyl percarbonate; tert.-butyl peracetate, tert.-butyl peroctanoate, tert.-butyl perpivalate; dialkyl peroxidicarbonates, such as diisopropyl, diethylhexyl, dicyclohexyl and diethylcyclohexyl peroxidicarbonates, mixed anhydrides of organic sulfo peracids and organic acids, such as acetylcyclohexylsulfonyl peroxide; azo compounds known as polymerisation catalysts, such as azoisobutyric acid nitrile. In the case of polymerisation using aqueous phases it is possible to use, as well as the above-mentioned catalysts, peroxydisulfates, peroxydiphosphates, or perborates of potassium, sodium or ammonium, hydrogen peroxide, tert.-butyl hydroperoxide or other water-soluble peroxides, as well as mixtures of various catalysts, and peroxide catalysts may be used also in the presence of 0.01 to 1% by weight, calculated on the monomers, of one or more reducing substances capable of making up a redox catalyst system, such as, for example, sulfites, bisulfites, dithionites, thiosulfates, aldehyde sulfoxylates, such as, for example, sodium formaldehyde sulfoxylate. Optionally, the polymerisation may be carried out in the presence of 0.005 to 10 parts of metal per million parts of monomer, of readily soluble or sparingly soluble metal salts, for example, of copper, silver, iron or chromium.

Molecular weight regulators may be added before or during polymerisation. Examples of such regulators, include aliphatic aldehydes having 2 to 4 carbon atoms, chlorohydrocarbons and bromohydrocarbons such as, for example, dichloroethylene and trichloroethylene, chloroform bromoform, methylene chloride and mercaptans. Other substances which may be added include polymerisation auxiliaries, such as antioxidants, for example, 2,6-di-tert.-butyl-4-methylphenol, trisnonylphenyl phosphite; other additives, such as epoxidised oils, for example, soya bean oil; fatty alcohols or fatty acid esters or auxiliaries for further processing of the polymer, such as, for example, known lubricants, waxes, heat and light stabilizers, plasticizers and pigments. The last-mentioned auxiliaries for further processing may alternatively be added at the end of the polymerisation process, optionally in a dissolved, molten or dispersed state.

If polymerisation is carried out using an aqueous liquor, this may contain 0.01 to 1% by weight, preferably 0.05 to 0.3% by weight, calculated on the monomers, of one or more

protective colloids such as, for example, polyvinyl alcohol, optionally containing up to 70 mole % of acetyl groups, cellulose derivatives, such as water-soluble methyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, mixed cellulose ethers, for example methylhydroxypropyl cellulose; as well as gelatin, and also copolymers of maleic acid or the semi-esters thereof and styrenes.

Polymerisation in aqueous liquor can, furthermore be carried out in the presence of 0.01 to 5% by weight, calculated on the monomers, of one or more emulsifiers, the emulsifiers being introduced in admixture with the above-mentioned protective colloids. It is possible to use anionic, amphoteric, cationic and non-ionic emulsifiers. Examples of anionic emulsifiers which may be used include alkali metal salts, alkaline earth metal salts and ammonium salts of fatty acids, such as lauric acid, palmitic acid or stearic acid, of acid fatty alcohol sulfuric acid esters, of paraffin-sulfo acids, of alkylarylsulfo acids, such as dodecylbenzenesulfo acid or dibutyl-naphthalenesulfo acid, of sulfosuccinic acid dialkyl esters, and the alkali metal and ammonium salts of epoxy group-containing fatty acids, such as epoxystearic acid, of reaction products of peracids, for example, peracetic acid with unsaturated fatty acids, such as oleic acid or linoleic acid, or unsaturated hydroxy fatty acids, such as ricinoleic acid. Examples of amphoteric or cation-active emulsifiers include: alkyl betaines, such as dodecyl betaine, and alkylpyridinium salts, such as hydroxyethyl-dodecylammonium chloride. Examples of non-ionic emulsifiers include partial fatty acid esters of polyhydric alcohols, such as glycerylmonostearate, sorbitol monolaurate, leate or palmitate, polyoxyethylene ethers of fatty alcohols or aromatic hydroxy compounds; polyoxyethylene esters of fatty acids as well as polypropylene oxide-, polyethylene oxide condensation products.

Other substances may be added to the polymer product after polymerisation, such as, for example, the processing auxiliaries mentioned above for stabilising and improving the properties of the polymers for further processing, optionally before or after separating the aqueous liquor.

For the treatment according to the invention the vinyl chloride polymer compositions may contain up to 50% by weight, more especially up to 20% by weight, calculated on the total composition, of compounds other than polymerised vinyl chloride. Such compounds may, for example, be monomeric vinyl chloride as well as other monomers used for polymerisation, polymerisation auxiliaries as well as, optionally, further processing auxiliaries, for example, those mentioned above; polymers not containing vinyl chloride, such as impact strength modifiers, polymeric additives for improving the flow properties and processing

properties and/or the heat resistance, and pigments.

The heat treatment is advantageously carried out in the presence of one or more inert gases such as, for example, air, nitrogen or water-vapor.

During this heat treatment it is advantageous for the polymer powder and/or the gas phase to be in motion, in order to achieve intensive contact of the two phases with one another. Such motion may be produced by mechanical or pneumatic means, for example, stirring, causing turbulence in the powder, allowing the powder to trickle down or spraying the powder in the gas chamber, and an additional relative speed with respect to the solid particles may optionally be given to the gas, for example in such a manner that the gas flows through a substantially loose layer of powder, preferably upwards from below.

The treatment according to the invention is advantageously carried out in the polymerisation vessel after removing the main quantity of liquid or gaseous reactants, or in one or more series-connected devices, for example, a down pipe or flow pipe, a high-speed mixer, a revolving tube advantageously provided on the inside with scoops, or a cyclone, it being possible for both the gas and the polymer to be circulated. Advantageously a device is used in which the polymer is guided, in a rotationally symmetric apparatus, in several flow rings arranged one above the other, by means of the tangential introduction of gas using appropriate fittings, or a fluidised bed or vortex bed is used.

The process according to the invention makes it possible to subject vinyl chloride polymers, and especially those that have been produced at 30 to 85°C by a bulk polymerisation process, to a sufficiently intensive temperature treatment to remove harmful residual monomers, for example, vinyl chloride, without at the same time causing marked discoloration of the material which would impair its further use. The treated polymers, contrary to those not treated, do not exhibit any impairment of the properties important for processing and use. The process may be carried out on a continuous basis and is not very liable to failure.

The temperature can be adjusted optimally to the desired treatment effect, thereby guaranteeing an intensive but careful treatment. The necessary devices are relatively simple to construct, sturdy and require little space. In particular, the treatment of the polymer in the polymerisation vessel necessitates only very low investment costs.

The following Examples are intended to illustrate the invention in detail. The results of measurements listed therein were determined as follows:

K value:

According to DIN 53 726, solvent: cyclohexanone. 65

VC residual monomer content:

Determined by gas chromatography according to the "head-space" method (Zeitschrift für Analytische Chemie 255 (1971) pages 345 to 350). 70

Discoloration test:

Polymer	100 parts	
Di-n-octyltin-bis-thioacetic acid ethylhexyl ester	1.5 parts	75
Lubricant mixture, consisting of hydrogenated castor oil, triglyceride and monoglyceride, (obtainable under the Trade Mark Loxiol GH 4)	0.7 parts	80
Montanic acid ester of 1,3-butanediol	0.3 parts	

The components are thoroughly mixed mechanically without heating and 300 grams of the mixture are plasticized for three minutes on a laboratory rolling mill with two rollers, whilst applying heat, to form a 3 mm thick rolled sheet. 85

Technical data:

Roller diameter	150 mm	90
Speed of rollers	11 revs/min	
Roller temperature	175°C	

After cooling the rolled sheet, rectangular portions of 10×12 cm are cut out of the sheet. 12 of these portions are placed into a compression mould with internal dimensions of 11×12.5 cm, which is arranged in a plate press heated to 175°C. The rolled sheet portions are pre-heated under slight pressure for 3.5 minutes then, for a period of ½ minute, the full pressure of 40 N cm² is applied, after a further 4 minutes cooling is effected with water under pressure to room temperature, the pressure is relaxed, the pressed plate is removed from the mould and observing the edge of the plate against a uniformly light, neutral white background, the color number is visually determined in accordance with a 5 part notation scale: 105

Notation 1:

Color as standard (usually faintly yellowish) 110

Notation 2:

Slightly discolored (yellowish)

Notation 3:

Clearly discolored (strong yellow color or reddish yellow) 115

Notation 4:

Strongly discolored (brown-yellow to orange-yellow)

Notation 5:

Very strongly discolored (light brown or orange red).

The standard used was a vinyl chloride homopolymer produced according to the bulk process having a K-value of 57, as yielded by polymerisation without subsequent heat treatment of the polymer and having a residual vinyl chloride content of 1% by weight (calculated on the polymer).

Example 1.

100 grams of diglycol and 500 grams of water are mixed in a high-speed mixer for 3 minutes with 10 kg of a vinyl chloride homopolymer, produced by bulk polymerisation at 69°C, having a K-value of 57 and a residual vinyl chloride content of 1% by weight (calculated on the polymer), and then the mixture is treated for 3 hours at 85°C in a circulating air drying chamber and subsequently cooled. At the end of the heat treatment 10093 grams of polymer are obtained.

A sample of the powder yielded by the heat treatment was dissolved in tetrahydrofuran, subjected to a silylation reaction with bis-trimethylsilyl - trifluoroacetamide analogously to the method described in the book by Allan E. Pierce "Silylation of organic compounds", Publishers: Pierce Chemical Comp., Rockford/III, U.S.A., 1968, page 72 *et seq.*; the polymer was then precipitated from the solution with methanol and the tetrahydrofuran-methanol mixture examined by gas chromatography. A silylation product of the diglycol could not be detected.

The determination of the residual vinyl chloride (VC)-content is carried out by gas chromatography according to the "head-space" method (see above) at 7 parts per 1 million parts (=PPM) of dry polymer. The discoloration test resulted in the notation 1.5.

For the purpose of better comparison the values determined are listed in the following table.

Comparison experiment A:

The procedure is as in Example 1, using the same bulk polymer but with the difference that the diglycol-water mixture is not added. The values determined are listed in the following table.

Comparison experiment B:

The procedure is as in Example 1, using the same bulk polymer, but with the difference that only 500 grams of water, without diglycol, are added to 10 kg of polymer.

Comparison experiment C:

The procedure is as in Example 1, using the same bulk polymer, but with the difference that instead of the mixture of diglycol and water, a mixture of 100 grams of phenol and

500 grams of water is added to 10 kg of polymer. The values determined are listed in the following table.

Example 2.

A bulk polymer of vinyl chloride is produced according to the 2-stage seed technique, wherein before the main polymerisation (second stage) 1% by weight (calculated on the total amount of vinyl chloride used in both stages) of diglycol is added to the reaction mixture and polymerisation is then effected at 62°C.

The main quantity of the excess, unreacted vinyl chloride is removed from the polymer produced by evacuating three times to approximately 50 torr. After this treatment the polymer still contains 0.2% by weight of monomeric vinyl chloride and has a K-value of 60. 10 kg of the polymer thus produced are then treated for 300 minutes at 85°C under normal pressure in a circulating air drying chamber, and subsequently cooled. The values measured are listed in the following table.

Examples 3—5.

Are carried out as in Example 1, but varying quantities of diglycol-water mixture are added to the polymer.

in Example 3: 400 grams of diglycol and 1000 grams of water

in Example 4: 10 grams of diglycol and 100 grams of water

in Example 5: 5 grams of diglycol and 100 grams of water.

Example 6.

100 grams of 1,6-hexanediol and 500 grams of water are mixed for 3 minutes in a high-speed mixer with 10 kg of a vinyl chloride homopolymer produced by bulk polymerisation at 55°C having a K-value of 67 and a residual vinyl chloride content of 0.3% by weight (calculated on the dry polymer), and the mixture is then treated for 50 minutes at 92°C in a circulating air drying chamber and subsequently cooled. The values measured are listed in the following table.

Example 7.

A mixture of 100 grams 2-butene-1,4-diol and 500 grams of water is added to 10 kg of a vinyl chloride homopolymer produced by bulk polymerisation at 62°C having a K-value of 60 and a residual vinyl chloride content of 0.2% by weight (calculated on the dry polymer).

In a pressure-tight cylindrical vessel of 40 liters capacity having an oil-heated double jacket and an anchor mixer passing along the wall, of which the mixer blades, curve in the shape of screws, are approximately 5 cm wide, brush the entire based and approximately 80% of the side walls of the vessel and rotate at

60 rev/min, the polymer to which the above-described mixture has been added is treated for 90 minutes at a pressure of 250 torr. The temperature of the heating oil is 92°C, the temperature of the polymer is measured at 85°C. During the treatment a weak air current is passed through the vessel.

After 90 minutes, the reduced pressure is removed and cooling is effected. The values measured are listed in the following table.

Example 8.

In the same apparatus as is described in Example 7, a mixture of 200 grams of 1,10-decanediol and 500 grams of ethanol is added to 10 kg of a vinyl chloride homopolymer produced by bulk polymerisation at 69°C, and the mixture is treated for 120 minutes at a product temperature of 97°C, a pressure of 100 torr and a stirrer speed of 60 rev/min whilst passing through a weak air current, then the reduced pressure is removed and cooling is carried out. The values measured are listed in the following table.

Example 9.

A mixture of 200 grams of a polyglycol of the average formula $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{11}\text{H}$ and 500 grams of water is added to 10 kg of a vinyl chloride homopolymer produced by bulk polymerisation at 62°C, having a K-value of 60 and a residual vinyl chloride content of 0.2% by weight (calculated on dry polymer), the mixture is mixed for 3 minutes in a high-speed mixer, then treated for 280 minutes at

75°C in a circulating air drying chamber and subsequently cooled. The values measured are listed in the following table.

Example 10.

The procedure is as in Example 1, using the same polymer, but instead of diglycol-water, a mixture of 50 grams of 1,3-propanediol and 500 grams of water is added. The heat treatment at 85°C is only 120 minutes long. The values measured are listed in the following table.

Example 11.

The procedure is as in Example 8, using the same polymer, but instead of decanediol-ethanol, a mixture of 100 grams of 1,4-butanediol and 500 grams of water is added. The heat treatment is effected at a product temperature of 90°C. The values measured are listed in the following table.

Example 12.

The procedure is as in Example 1, using the same polymer, except that instead of diglycol-water, a mixture of 200 grams of neopentylglycol and 500 grams of water is added. The values measured are listed in the following table.

In the table:

VC = vinyl chloride

min = minutes

PPM = parts per 1 million parts of dry polymer.

TABLE

Example or Comparison Experiment	Polymer K-value	Compound added	Quantity % by weight	Heat treatment				Residual VC content PPM	Colour number
				Temp. °C	Pressure	Duration min	Product °C.h		
Comp. A	57	—	—	85	1 atm	180	255	10	4
Comp. B	57	Water	5	85	1 atm	180	255	8	4
Comp. C	57	Phenol	1	85	1 atm	180	255	11	4
Ex. 1	57	Diglykol	1	85	1 atm	180	255	7	1.5
Ex. 2	60	"	1	85	1 atm	300	425	1	1
Ex. 3	57	"	4	85	1 atm	180	255	5	2.5
Ex. 4	57	"	0.1	85	1 atm	180	255	6	2.5
Ex. 5	57	"	0.05	85	1 atm	180	255	8	3
Ex. 6	67	1,6-Hexanediol	1	92	1 atm	50	77	15	1.5
Ex. 7	60	2-Butene-1,4-diol	1	85	250 torr	90	127.5	21	1
Ex. 8	57	1,10-Decanediol	2	97	100 torr	120	194	9	2

TABLE (Continued)

Example or Comparison Experiment	Polymer K-value	Compound added	Quantity % by weight	Heat treatment				Residual VC content PPM	Colour number
				Temp. °C	Pressure	Duration min	Product °C.h		
Ex. 9	60	Polyglykol n - 11	2	75	1 atm	280	350	6	2.5
Ex. 10	57	1,3-Propanediol	0.5	85	1 atm	120	170	24	2
Ex. 11	57	1,4-Butanediol	1	90	100 torr	120	180	10	1.5
Ex. 12	57	Neopentylglycol	2	85	1 atm	180	255	7	2

WHAT WE CLAIM IS:—

1. A process for the treatment of a polymer composition comprising a homo-, co- or graft polymer product containing at least 50% by weight of polymerised vinyl chloride units (based on the total weight of the composition) and the composition including monomeric material and optionally water, which process comprises removing from the composition the main quantity of unreacted monomeric material and, if present, water, and thereafter subjecting the composition in a particulate state to a heat treatment to reduce its residual content of vinyl chloride monomer, the heat treatment being carried out at a temperature in the range of from 75° to 120°C for a period of from 10 minutes to 6 hours and in the presence of a total of from 0.01 to 5% by weight (based on the dry polymer product) of at least one aliphatic, saturated or unsaturated, branched or unbranched compound

which contains two or more free hydroxyl groups and at least two carbon atoms and which, in the case of a compound containing four or more carbon atoms, may contain at least one C—O—C link.

2. A process as claimed in claim 1 wherein the aliphatic compound contains no more than 24 carbon atoms.

3. A process as claimed in claim 1 or claim 2, wherein the heat treatment is carried out at atmospheric pressure or under reduced pressure.

4. A process as claimed in claim 3, wherein the heat treatment is carried out at a pressure in the range of from 50 to 760 Torr.

5. A process as claimed in any one of claims 1 to 4, wherein the heat treatment is carried out in an atmosphere comprising one or more of air, nitrogen and water vapor.

6. A process as claimed in claim 5, wherein the atmosphere comprises air.

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7. A process as claimed in any one of claims 1 to 6, wherein the heat treatment is carried out at a temperature in the range of from 80° to 100°C.
- 5 8. A process as claimed in any one of claims 1 to 7, wherein the product of the average treatment temperature (°C.) and treatment duration (hours) is in the range of from 25 to 350 (°C.h).
- 10 9. A process as claimed in claim 8, wherein the said product is in the range of from 50 to 260 (°C.h).
10. A process as claimed in any one of claims 1 to 9, wherein the heat treatment is carried out in the presence of a total of from 0.2 to 2% by weight of the aliphatic compound or compounds (based on the dry polymer product).
- 15 11. A process as claimed in claim 10, wherein the said total is in the range of from 0.5 to 1.5%.
12. A process as claimed in any one of claims 1 to 11, wherein the or at least one of the aliphatic compounds has the general
- 25 formula



in which X represents H or CH₃, and n represents an integer of from 1 to 12.

13. A process as claimed in any one of claims 1 to 11, wherein the or at least one aliphatic compound is diglycol or triglycol, or the heat treatment is carried out in the presence of a mixture of diglycol and triglycol.
14. A process as claimed in any one of claims 1 to 11, wherein the heat treatment is carried out in the presence of 2-butene-1,4-diol.
15. A process as claimed in any one of claims 1 to 12 wherein the or at least one

aliphatic compound has from 3 to 12 carbon atoms and no C—O—C link.

16. A process as claimed in any one of claims 1 to 15, wherein the polymer product has been obtained by gas-phase polymerisation.

17. A process as claimed in any one of claims 1 to 16, wherein the polymer product has been obtained by liquid-phase bulk polymerisation.

18. A process as claimed in claim 17, wherein the polymer product has been obtained by a bulk polymerisation carried out at a temperature in the range of from 30° to 85°C.

19. A process as claimed in any one of claims 1 to 18, wherein the polymer composition contains at least 80% by weight of polymerised vinyl chloride units (calculated on the total composition).

20. A process as claimed in claim 19, wherein the proportion of polymerised vinyl chloride units is at least 98% by weight (calculated on total composition).

21. A process as claimed in any one of claims 1 to 20, wherein, prior to the heat treatment, the polymer product contains from 0.1 to 1% by weight of residual monomeric material.

22. A process as claimed in any one of claims 1 to 21, wherein, after the heat treatment, the polymer product contains not more than 0.001% by weight of residual vinyl chloride monomer.

23. A process as claimed in claim 1, conducted substantially as described in any one of the Examples herein.

24. A homo-, co- or graft polymer containing at least 50% by weight of polymerised vinyl chloride units, whenever treated by a process as claimed in any one of claims 1 to 23.

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